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Mechanical milling-induced room-temperature ferromagnetic phase in MnO_2–ZnO system

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Mechanical milling of a mixture of powders composed of 2 mol % MnO_2 and 98 mol % ZnO leads to a ferromagnetic phase with Curie temperature above 300 K. The magnetic field dependence of magnetization manifests a residual magnetization of 2.84×10^{-4} emu/g and a coercive force of 76 Oe at 300 K; the residual magnetization of the as-milled sample is larger than those of heat-treated samples. It is speculated that the ferromagnetic behavior is imposed to Zn-doped manganese oxide phases formed on the surface of MnO_2 particles via the mechanical milling. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2234269]

Magnetic semiconductors have attracted considerable attention from a point of view of application to spin electronic devices. One of the potential magnetic semiconductors is ZnO doped with manganese ion. A theoretical model based on Zener mechanism predicted that ZnO would exhibit ferromagnetism with Curie temperature higher than 300 K when *p*-type semiconductor of ZnO doped with 5% of Mn would be formed.[1] This theoretical prediction accelerated the following experimental studies on magnetic properties of Mn–Zn–O system. Sharma *et al.*[2] reported ferromagnetic behavior at room temperature for bulk polycrystalline materials as well as thin films prepared from 98 mol % ZnO and 2 mol % MnO_2 powders. They observed that the saturation magnetization increases as the sintering temperature is decreased from 900 to 500 °C for the bulk materials. Their conclusion is that bulk polycrystalline materials of ZnO in which manganese ions are homogeneously dispersed show ferromagnetism with Curie temperature above 425 K, and that the decrease in magnetization with an increase in sintering temperature is attributed to clustering of manganese at higher temperatures.

In contrast, Kundaliya *et al.*[3] examined the structure and magnetic properties of not only bulk polycrystalline materials obtained from ZnO and MnO_2 but also thin film bilayers composed of ZnO and Mn_3O_4, and deduced conclusions different than those derived by Sharma *et al.*[2] Kundaliya *et al.*[3] suggested that the ferromagnetism originates in metastable $Mn_{2-x}Zn_xO_{3-\delta}$ phase. In the bulk materials, the ferromagnetic phase is formed in the interface region between particles of ZnO and Mn_2O_3 converted from MnO_2 by the heat treatment process. In other words, Mn ion is not homogeneously distributed in the ZnO matrix. García *et al.*[4] explored crystalline phase and valence state of Mn in samples prepared by mixing ZnO with MnO_2 and annealing at 500–800 °C. They proposed that the room-temperature ferromagnetism is caused by Zn-doped Mn_2O_3 formed on the surface of MnO_2 particles, and argued that the mechanism of ferromagnetism is the double exchange interaction among Mn^{4+} and Mn^{3+} ions. Bhatti *et al.*[5] also deduced a conclusion that the ferromagnetism in $(ZnO)_{0.98}(MnO_2)_{0.02}$ is ascribable to some impurity phase.

On the other hand, Blythe *et al.*[6] discovered an interesting phenomenon that a room-temperature ferromagnetic phase was obtained only via mechanical alloying of a mixture composed of ZnO and MnO_2 powders. They found that the magnetization at room temperature monotonically increased with an increase in the alloying time, although clarification of low-temperature magnetic properties as well as identification of crystalline phase has not been carried out. The fact that only mechanical milling can lead to formation of ferromagnetic phase in the ZnO–MnO_2 system is very intriguing, and it is of great importance from both fundamental and practical viewpoints to obtain further detailed information concerning the room-temperature ferromagnetic phase. In the present investigation, we report on some new information about crystalline phase and magnetism in the mechanical milling-induced MnO_2–ZnO system.

For sample preparation, MnO_2 (β-type structure, 99.9%, Mitsuwa Chemicals Co., Ltd.) and ZnO (99.99%, Kojundo Chemical Laboratory Co., Ltd.) were used as raw materials. Beforehand commercially available MnO_2 powders were pulverized via mechanical milling for 24 h with a planetary ball mill composed of a container and balls made of agate. Powders of MnO_2 thus obtained and ZnO were weighed so that the resultant sample would contain 2 mol % MnO_2 and 98 mol % ZnO. After 10 g of mixed powders along with 20 ml of acetone were put into the container, the mechanical milling was performed for 24 h. The volume of the container was 45 ml. The average diameter of the balls was 12 mm and the number of the balls used was 7. After the mechanical milling, the resultant powders were dried in air, and calcined at 100–700 °C for 8 h. The powders thus obtained were pressed under a static pressure to fabricate a pellet, and heat treated for 12 h at the same temperature as the calcination temperature. The heat-treated samples as well as the powders just after the mechanical milling were subjected to x-ray diffraction (XRD) analyses with Cu K_α radiation (Rigaku RINT2500) to identify crystalline phases. Magnetic properties of the samples were measured by using a superconducting quantum interference device magnetometer (Quantum Design, MPMS2).

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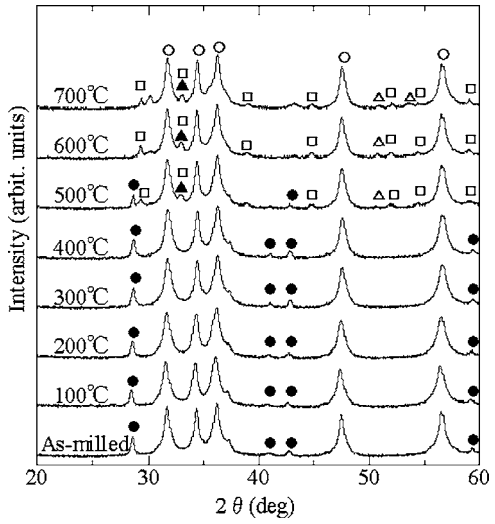

FIG. 1. X-ray diffraction patterns for mechanical milling-induced sample and those heat treated at 100–700 °C. The diffraction lines can be assigned to ZnO (open circles), MnO_2 (solid circles), $ZnMn_2O_4$ (open squares), Mn_3O_4 (open triangles), and Mn_2O_3 (solid triangles).

Figure 1 depicts XRD patterns for the mechanical milling-induced and heat-treated samples. In ordinate of the figure, the logarithmic diffraction intensity is shown. In addition to intense diffraction lines assigned to ZnO, diffraction lines attributed to manganese oxides are observed. A crystalline phase containing manganese is only MnO_2 for the sample just after the mechanical milling and those heat treated below 400 °C, while other crystalline phases such as $ZnMn_2O_4$, Mn_3O_4, and Mn_2O_3 are precipitated in the samples heat treated above 500 °C. It should be noted that these oxides plausibly show nonstoichiometry and/or contain a small amount of impurity ions.

Figure 2 shows magnetization at 300 K as a function of magnetic field for powders just after the mechanical milling as well as samples heat treated at 100–400 °C [Fig. 2(a)] and samples heat treated at 500–700 °C [Fig. 2(b)]. The meanings of the symbols are given in the figures. In the ordinate, the magnetization per total mass for the samples is plotted. The magnetization curve for the as-milled sample clearly exhibits a hysteresis loop, as shown in Fig. 2(c), where the magnetization curves at −1000 to 1000 Oe are illustrated; the residual magnetization and the coercive force are estimated to be 2.84×10^{-4} emu/g and 76 Oe, respectively. The dependence of magnetization on magnetic field for not only the sample just after the mechanical milling but also those heat treated below 600 °C manifests ferromagnetic behavior, whereas the sample heat treated at 700 °C is paramagnetic at 300 K, as shown in Fig. 2(b). It is clearly seen in Fig. 2(a) that the magnetization of the as-milled sample is larger than those heat treated below 400 °C as far as the magnetic field lies within ±10 kOe. Moreover, the residual magnetization of the as-milled sample is larger than that of the sample heat treated at 500 °C, as shown in Fig. 2(c). We also carried out magnetization measurements at 300 K for MnO_2 powders before and after mechanical milling for 24 h. The variation of magnetization with magnetic field for MnO_2 powders after mechanical milling, as shown in Fig. 2(d), confirms that MnO_2 is paramagnetic at 300 K even after the mechanical milling. A similar result was obtained for MnO_2 before the mechanical milling. Furthermore, we attempted to observe ferromagnetic behavior for as-

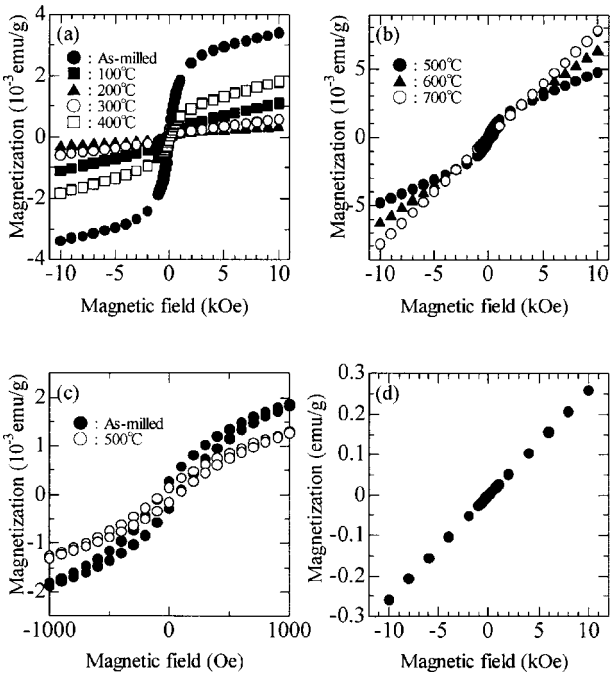

FIG. 2. Dependence of magnetization at 300 K on magnetic field for (a) as-milled sample as well as those heat treated below 400 °C and (b) samples heat treated at 500–700 °C. (c) The magnetization as a function of magnetic field in a narrow range for as-milled sample and that heat treated at 500 °C. (d) Dependence of magnetization at 300 K on magnetic field for as-milled MnO_2 powders.

milled sample composed of 5 mol % MnO_2 and 95 mol % ZnO, but the resultant sample only showed paramagnetic behavior at 300 K. These facts indicate that the coexistence of a large amount of ZnO with MnO_2 is indispensable for the appearance of room-temperature ferromagnetic phase.

In Fig. 3 are shown temperature variations of field-cooled and zero-field-cooled magnetizations under a magnetic field of 50 Oe for the sample derived by the mechanical milling. A gradual increase in both field-cooled and zero-field-cooled magnetizations with a decrease in temperature is displayed, suggesting that the as-milled sample includes a ferromagnetic component with Curie temperature higher than room temperature. The discrepancy between the field-

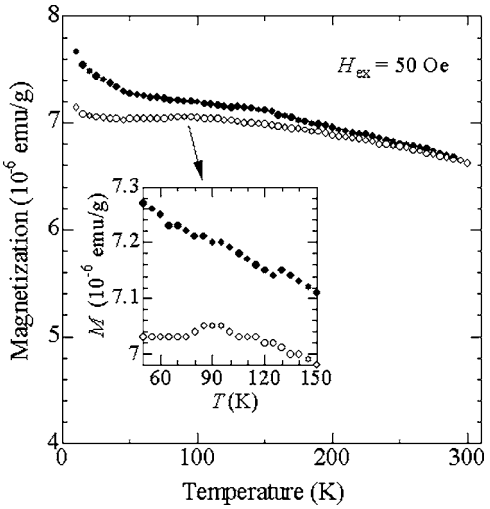

FIG. 3. Temperature dependence of magnetization for the as-milled sample. Both field cooling (●) and zero-field cooling (○) were carried out. H_{ex} denotes the magnetic field applied.

cooled and zero-field-cooled magnetizations is explainable in terms of the superparamagnetism. A close look at the temperature dependence of zero-field-cooled magnetization reveals that the magnetization takes a slight maximum at around 90 K as illustrated in the inset of Fig. 3. This temperature corresponds to the Néel temperature of MnO_2.

We must refer to contamination which may bring about the ferromagnetic behavior observed, because the ball milling process inevitably causes the contamination by some impurities from the balls and the container used for milling. In the present study, we have used the container and balls made of agate as described above. The main constituent of the agate is SiO_2, and the content exceeds 99.9%. Magnetic impurities in the agate are iron oxide and manganese oxide, but the concentration of them is as low as 0.01%. We have performed the mechanical milling of diamagnetic materials such as SiO_2 as well as ZnO under the same conditions as mentioned above, but the resultant powders exhibited only diamagnetic behavior. Hence, we can rule out the possibility that the contamination by foreign magnetic phases brings about the ferromagnetic behavior observed for the mechanical milling-induced sample.

As well known, the mechanical alloying,[7] i.e., the solid-state reaction via mechanical milling, has been effectively utilized for fabrication of materials such as alloys, oxides, sulfides, and so forth. For instance, the mechanical milling of $ZnFe_2O_4$ particles renders them ferrimagnets although a stable phase of $ZnFe_2O_4$ is antiferromagnetic with the Néel temperature of 10 K.[8,9] The mechanical milling was also utilized to synthesize nanocrystalline $ZnFe_2O_4$ from ZnO and Fe_2O_3.[10] In the present study, it is reasonable to infer that the mechanical milling process facilitates the solid-state reaction between MnO_2 and ZnO particles to form new crystalline phases, which manifest the room-temperature ferromagnetic behavior. Although only MnO_2 and ZnO are detected in the XRD pattern, as shown in Fig. 1, we speculate that only the surface region of MnO_2 particles is converted into Zn-doped manganese oxide containing both Mn^{4+} and Mn^{3+} like the compound suggested by García *et al.*,[4] leading to ferromagnetism due to the double exchange interaction among Mn^{4+} and Mn^{3+} ions. Nonetheless, further detailed study about valence states and distributions of manganese ions on the surface of MnO_2 is necessary. The interpretation that the ferromagnetic phase is present only in the surface region of MnO_2 particles is coincident with the superparamagnetic behavior suggested in Fig. 3.

It is curious that the heat treatment of the as-milled sample at lower temperatures such as 100–400 °C rather decreases the magnetization, as shown in Fig. 2(a). As shown in Fig. 1, the crystalline phases are independent of the heat treatment temperature below 400 °C. However, a slight variation of lattice constant of MnO_2 with the heat treatment is recognized; the diffraction line at around $2\theta = 28.5° - 28.7°$ assigned to MnO_2 is shifted to a higher diffraction angle side as the heat treatment temperature is increased, and the position of the diffraction line is different between the as-milled sample and the heat-treated ones. Previous studies using thermogravimetry on a mixture of 2 mol % MnO_2 and 98 mol % ZnO revealed that reduction of Mn^{4+} into Mn^{3+} took place even at low temperatures such as 200 °C.[3,4] The oxidation state of manganese ions in the surface phase on the MnO_2 particles is possibly changed during the heat treatment at low temperatures, and thereby the magnetization as well as the lattice constant is varied with the heat treatment temperature. Further investigation about the valence state of manganese ion in the present samples, which is inevitable for thorough clarification of mechanism of the ferromagnetic behavior as mentioned above, is in progress.

In conclusion, the room-temperature magnetization as a function of magnetic field and the temperature dependence of magnetization confirm that the room-temperature ferromagnetic phase could be formed by only mechanical milling of MnO_2 and ZnO powders without any postannealing at elevated temperatures as far as the relative amount of ZnO to MnO_2 was large enough. One of the most interesting results is that the residual magnetization is larger for the as-milled sample than for the heat-treated ones. It is thought that the ferromagnetic phase is predominantly based on Zn-doped manganese oxide formed in the interface region between MnO_2 and ZnO particles.

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